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(54) Title: METHOD TO IMPROVE ADHESION OF A THIN SUBMICRON FLUOROPOLYMER FILM ON AN ELECTRONIC DEVICE			
(57) Abstract			
The present invention comprises a substrate having at least one of metal, alloy, or semiconductor features with an insulative fluoropolymer dielectric layer bonded thereto through the use of silane coatings, and a method of manufacture.			

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TITLE OF THE INVENTION

METHOD TO IMPROVE ADHESION OF A THIN SUBMICRON
FLUOROPOLYMER FILM ON AN ELECTRONIC DEVICE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Application Serial No.08/834,788 filed April 3, 1997.

FIELD OF THE INVENTION

The present invention relates to dielectric layers of electronic components, such as integrated circuits. More specifically, the present invention relates to a method of increasing the adhesion properties of low dielectric constant material on electronic components and the resulting articles by using an adhesion promoter.

BACKGROUND OF THE INVENTION

Integrated circuits are created from a semiconductor wafer using various etching, doping, and depositing steps that are well known in the art of fabricating integrated circuit devices. The wafer may be comprised of a number of integrated circuit die that each represent a single integrated circuit chip. Modern high-performance integrated circuits are comprised of millions of transistors that perform functions such as random access memory, central processing communications, etc. Each of these transistors must be interconnected with electrically-conducting elements. A typical modern integrated circuit now contains multiple layers of these conductor elements. Due to the size constraints of placing millions of conducting elements on a chip that has an area of only a few square centimeters, the connecting elements themselves have become very small, and the distance that separates conducting elements has shrunk as well. A state-of-the-art integrated circuit produced today has a conductor width of 0.25 microns and conductor spacing of 0.25 microns.

Because of the small spacing, many electrical performance problems are now arising in integrated circuits. The reduced spacing results in increased electrical capacitances which cause capacitive interconnect delay and can slow down the operation speed of the circuit. Capacitance also causes cross-talk which can result in signal errors being generated if the problem is not solved. In addition, it is also desirable to reduce the capacitance in order to reduce the amount of power that the integrated circuit requires to operate.

Since the dimensions of the integrated circuit are constrained, for example, at 0.25 microns for the current device technology generation and decreasing to as little as 0.07 microns in 10 years, the only way to reduce the capacitance between the conducting elements is to use an insulative material with a low dielectric constant. Conventional semiconductor fabrication commonly uses silicon dioxide as a dielectric, which has a dielectric constant of about 3.9. The lowest possible or ideal dielectric constant is 1.0, which is the dielectric constant of a vacuum, whereas air has a dielectric constant of less than 1.001.

Polytetrafluoroethylene (PTFE) has the lowest dielectric constant (2.0) of any non-porous material that also has the thermal stability to withstand the rigors of the integrated circuit manufacturing process. A typical integrated circuit manufacturing process comprises approximately 360 process steps. Many of these steps involve temperature excursions which can cause severe stresses on the materials within the integrated circuit. These stresses are caused when two adjacent materials in the integrated circuit structure have differing coefficients of thermal expansion. As a wafer is heated up or cooled down, one component of the integrated circuit will shrink or expand more or less than its adjacent component. This causes interfacial shear stress between the two components, say, for example, a metal electrically conducting element and a polymeric dielectric insulating element. Another way in which high interfacial shear stresses are generated in integrated circuit manufacturing is during the chemical mechanical polishing (CMP) process. This process is used to polish a wafer flat for subsequent high resolution photolithographic processing. In the CMP process, the wafer is placed face down onto a rotating platen in the presence of a corrosive slurry. This corrosive slurry polishes away the disparities on the surface of the wafer. Since high levels of force are used to press the wafer down onto the rotating platen for polishing, significant interfacial shear stresses are generated. If the interfacial shear stress generated by these forces exceeds the adhesive strength of the interface, the interfaces will separate. This interfacial separation, commonly referred to as delamination, weakens the mechanical and electrical integrity of the integrated circuit and also renders it susceptible to corrosion. It is therefore apparent that any dielectric material used in an integrated circuit must successfully withstand the rigors of thermal excursions and chemical mechanical polishing.

Previous attempts to improve the adhesion of PTFE have used techniques such as mechanical roughening of the surface or the use of discrete adhesive layers. Such techniques are not applicable to integrated circuits because of the exceedingly small sub-micron feature size of the integrated circuit. It is not feasible to provide either a mechanical roughening or a discrete adhesion layer.

SUMMARY OF THE INVENTION

The present invention relates to an article containing at least one layer of a low dielectric constant material where resistance to delamination is increased by using an adhesion promoter. The present invention also relates to a method for increasing the adhesion of low dielectric constant material to electronic components. This method comprises the following steps: treating a substrate bearing at least one of metal and semiconductor components with an alkoxy silane or silazane; coating the treated substrate with a fluid dispersion containing fluoropolymer dielectric material having a weight loss of less than 0.15 %/minute at 420 °C; and forming a dielectric layer having a thickness of less than 5µm.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a scanning electron micrograph (SEM) cross-section of a 0.75 micron PTFE film.

Figure 2 is an SEM surface view of a single crystal silicon wafer which has been coated with a bicontinuous PTFE microemulsion.

Figure 3 is a graph of Deposited Film Thickness (Angstroms) v. Spin Speed (RPM).

Figure 4 is a graph of Isothermal Weight Loss Rate (%/minute) v. Temperature.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises a method for bonding at least one dielectric fluoropolymer layer to the surface of an electronic component, such as a semiconductor wafer or an integrated circuit device. The semiconductor wafer is usually formed from SiO₂, but could also be formed from any other suitable material such as, germanium, silicon, germanium, silicon carbide, gallium arsenide, selenium, tellurium, InSb, BP, CdS, ZnSe, ZnTe, PbS, InP, PbSe, PbTe, InAs, GaSb, ZnS and Bi₂Te₃. The electronic component contains metal traces or conductive pads formed from well known materials such as nickel, copper, aluminum, any of the precious metals, gold, platinum, or any other suitable conductive metal or alloy.

The adhesive bond, i.e., resistance to delamination between the fluoropolymer and the integrated circuit substrate, is provided by an alkoxy silane or silazane. The integrated circuit structure which may be an active or passive device may contain one or more layers of low dielectric constant material of the present invention. These layers are formed from a

fluoropolymer dispersion, solution, or vapor. The dielectric properties are determined by subsequent processing.

As the term is used herein "fluoropolymer" means a polymer with a fully fluorinated structure. In a fully fluorinated polymer, essentially all of the hydrogen atoms are replaced by fluorine atoms.

As the term is used herein "fluorinated polymer" means a polymer with a partially fluorinated structure. In a partially fluorinated structure not all of the hydrogen atom are replaced by fluorine atoms.

As the term is used herein, low dielectric constant means a dielectric constant of between 1 and 2.5, preferably less than 2.2, and most preferably less than 1.9. By comparison, a conventional silicon dioxide dielectric material for use in integrated circuits has a dielectric constant of between 3.9 to 4.2. By having a dielectric constant of between 1 and 2.5, a dielectric layer formed by the teachings of the present invention forms an electrically insulating layer between two electrically conducting layers such as polysilicon or metal, which is effective in lowering the effective capacitance, reducing the cross-talk, and increasing the signal velocity of propagation of the conductive layers separated by the dielectric material.

As used herein, a fluoropolymer dispersion means a stable isotropic mixture of fluoropolymer particles, water, and surfactant. Other components such as a salt or cosurfactant (such as an alcohol, amine, or other amphiphilic molecule) may also be part of the dispersion formulation. The fluoropolymer particles in water reside in distinct domains separated by an interfacial layer rich in surfactant. Examples of such fluoropolymer dispersions are polytetrafluoroethylene (PTFE) dispersions such as Resin T-30 manufactured by DuPont and Resin D-2 manufactured by Daiken. Other PTFE and fluoropolymer dispersions may be used such as those described hereinafter. Fluoropolymer dispersions having particle sizes of less than 80 nanometers are interchangeably referred to herein as microemulsions, microdispersions, nanoemulsions or nanodispersions.

Other components, such as salt or a co-surfactant (such as an alcohol, amine, or other amphiphilic molecule) may also be part of the microemulsion formulation. The oil and water reside in distinct domains separated by an interfacial layer rich in surfactant. Because the domains of oil or water are so small, microemulsions appear visually transparent or translucent. Unlike emulsions, microemulsions are equilibrium phases.

Microemulsions can have several microstructures, depending upon composition, and sometimes upon temperature and pressure. There are three most common structures. One is an oil-in-water microemulsion where oil is contained inside distinct domains (droplets) in a

continuous water-rich domain. The second is water-in-oil microemulsion, so-called inverse microemulsions, where water is contained inside distinct domains (droplets) in a continuous oil-rich domain. The third is a bicontinuous microemulsion where there are sample-spanning intertwined paths of both oil and water, separated from each other by a surfactant-rich sponge-like structure.

ADHESION PROMOTER

Heretofore, it was believed that there were no known commercially-available adhesion promoters for PTFE thin films, especially for promoting adhesion of PTFE thin films to silicon dioxide coated substrates, such as those used in the manufacture of integrated circuits. Conventional methods of improving adhesion, such as mechanical roughening of a surface to be coated, are impractical because the feature size of both a PTFE thin film and the features on the substrate surface are less than 1 micron in size.

There are, however, commercially-available adhesion promoters for other thin films formed from non-fluoropolymer materials which are used in the semiconductor industry. For example, hexamethyldisilazane (HMDS) is commonly used as an adhesion promoter for photoresist. In addition, polyimide polymers use adhesion promoters based on aminopropyltriethoxysilane (APTS) or similar compounds. In both instances, the adhesion promoter is applied either by vacuum coating or by spin coating in a dilute solution followed by curing. The resulting layer of adhesion promoter typically has a thickness or sub-monolayer of up to 10 monolayers. These adhesion promoters typically contain functional alkoxy or silazane groups, which can bond to the SiO_2 surface, and end groups, such as amino groups, which allow for bonding of the polymer. There are, however, no known commercially-available adhesion promoters that can bond to a PTFE molecule due to the inert and non-reactive nature of the PTFE molecule. In fact, prior art teaches that silane coatings do not bond to fluoropolymer matrices. This is discussed in U.S. Patent No. 4,849,284.

In the present invention, it has been determined that alkoxy silane and silazane compounds, improve the bond of PTFE to SiO_2 substrates. There are two possible mechanisms for this. 1) Surface hydroxyl groups are displaced from the SiO_2 surface by the adhesion promoter, resulting in better wetting of the surface by the fluoropolymer and improved Van der Waals bonding. In essence, the adhesion promoter converts the surface from a hydrophilic surface to a hydrophobic surface. 2) Di, tri and tetra functional silanes or silazanes create a loose, open, crosslinked structure upon curing. This structure is

penetrated by the fluoropolymer, resulting in improved mechanical bonding. Suitable silanes or silazanes include:

aminopropyltrimethoxysilane,
aminopropyltriethoxysilane,
aminoethyltrimethoxysilane,
methylaminopropyltrimethoxysilane,
aminopropyltripropoxysilane,
aminopropylmethyldiethoxysilane,
aminopropylethyldiethoxysilane,
aminomethyltriethoxysilane,
aminoisobutyltrimethoxysilane,
aminobutyltriethoxysilane,
beta-aminoethyltriethoxysilane,
aminobutylmethyldiethoxysilane,
(aminoethylaminomethyl)-phenethyltrimethoxysilane,
(aminoethylaminomethyl)-phenethyltriethoxysilane,
n-(aminoethyl)-aminopropyl-methyldimethoxysilane,
n-(aminoethyl)-aminopropyl-methyldiethoxysilane,
n-(aminoethyl)-aminopropyl-trimethoxysilane,
n-(aminoethyl)-aminopropyl-triethoxysilane,
p-aminophenyltrimethoxysilane,
p-aminophenyltriethoxysilane,
n-phenylaminopropyltrimethoxysilane,
n-phenylaminopropyltriethoxysilane,
(trimethoxysilylpropyl)diethylenetriamine,
(triethoxysilylpropyl)diethylenetriamine,
phenylaminotriethoxysilane,
phenylaminotrimethoxysilane,
phenylaminotripropoxysilane,
hexamethyldisilazane,
tetraethoxysilane,
tetramethoxysilane, or
tetrapropoxysilane,

alone or in combination with one another.

PTFE NANOEMULSION/DISPERSION

Polymerization of emulsified and microemulsified unsaturated hydrocarbon monomers is known, where high reaction rates, high conversions and high molecular weights can be achieved. A microemulsion can be distinguished from a conventional emulsion by its optical clarity, low viscosity, small domain size, thermodynamic stability and spontaneous formation. Polymerization of microemulsified monomers has many advantages over traditional polymerization of emulsified monomers. Microemulsions are normally transparent to translucent so that they are particularly suitable for photochemical reactions, while emulsions are turbid and opaque. Also, the structural diversity of microemulsions (droplets and bicontinuous) is set by thermodynamics, and rapid polymerization may be able to capture some of the original structure. In addition, microemulsion polymerization enables the production of stable, monodisperse microlatexes containing colloidal particles smaller than those produced from classical emulsion polymerization processes. Smaller particle size improves the ability to form coatings without microcracking. The increased surface area improves particle fusion during molding operations.

Emulsion polymerization, as opposed to microemulsion polymerization, of dissolved gaseous tetrafluoroethylene (PTFE) or its copolymers is a known process. Aqueous colloidal dispersions of PTFE or its copolymers can be prepared in a pressure reactor by placing the gaseous monomer, or a mixture of monomers in contact with an aqueous solution containing at least one emulsifier which generally is a fluorinated surfactant, possibly a buffer for keeping the medium at a given pH, and at least an initiator which is capable of forming free radicals at the polymerization temperature. The free radical initiators can be water soluble peroxides, or alkaline or ammonium persulfates. Persulfate can be used alone if the polymerization temperature is above approximately 50°C, or in association with a reducing agent such as ferrous salt, silver nitrate, or sodium bisulfite if the polymerization temperature is approximately between 5 to 55°C, as described in the U.S. Patent No. 4,384,092, which is incorporated herein by reference.

The gaseous monomer molecules in the foregoing process enter the aqueous liquid and react to form polymer without first forming a distinct liquid phase. Thus, the polymer particles are large particles suspended in the aqueous mixture; and the process is not a true liquid-in-liquid emulsion polymerization. The process is sometimes referred to as dispersion polymerization.

Microemulsion polymerization operates by a different mechanism than emulsion polymerization. It involves polymerization of liquid monomer rather than gaseous monomers.

Because the polymerization involves polymerization of unusually small cells of liquid monomer, the resulting polymer particles are unusually small. However, polymerization of liquid TFE is not usually practiced because of the well known potential handling hazards.

The thickness of the dielectric layer or interlayer dielectric (ILD) formed in accordance with the teachings herein is in a range of from about 0.1 to about 5.0 μm . More typically, the thickness is in a range of from about 0.5 to about 1.5 μm . Such a range of thicknesses may be particularly desired for producing present and future generation integrated circuit structures.

The low dielectric material of the present invention is a fluoropolymer which may be deposited from a microemulsion or microdispersion comprising particles of approximately an average size of from about 1 to about 80 nanometers (0.001 to 0.080 micrometers), preferably from about 1 to about 60 nanometers, and most preferably from about 1 to about 30 nanometers; surfactant; and water. The fluoropolymer may include, but is not limited to, polytetrafluoroethylene (PTFE), fluorinated ethylenepropylene (FEP), fluoromethacrylate (Fac), or perfluoroalkoxy polymer (PFA).

The low dielectric material may have porosity induced in order to reduce its dielectric constant. The porosity may be created by employing a bicontinuous microemulsion. Such a bicontinuous fluoropolymer microemulsion system contains both oil (monomer) phase and aqueous phase intertwined into each other, separated by surfactant layers. A rapid polymerization of the monomers (oil phase) can capture the unpolymerized microstructure. When the water is removed during the drying step, a porous structure is left behind.

The low dielectric constant material of the present invention may be deposited to form an ILD by a spin coating process using a microemulsion liquid. The spin coating process is comprised of several steps which are outlined hereinafter:

- 1) A substrate containing an adhesion promoter layer, such as a silicone wafer containing a layer of APTS or HMDS, for example, is spun at about 50 RPM. While the substrate is spinning at such a speed, a wetting agent, such as isopropanol, is dispensed onto the surface of the spinning substrate to wet out the surface of the substrate.
- 2) The adhesion promoter is cured at 130°C for 60 seconds or at room temperature for 24 hours.
- 3) A fluoropolymer microemulsion is dispensed onto the surface of the spinning substrate, while it is spinning at 500 RPM.

4) The rotational speed of the substrate is next increased to a range of from about 1000 to about 5000 RPM. The rotational speed employed determines the thickness of the dielectric layer achieved, as best seen by reference to Figure 3.

5) The increased rotational speed is maintained, until the coating thickness of the microemulsion stabilizes. Typically, stabilization occurs in from 10 to about 50 seconds, depending on the rotational speed. In this regard, a faster speed requires less time to stabilize.

6) The coated substrate is initially baked at a temperature of about 200°C to drive off the water and surfactant of the microemulsion.

7) Thereafter, the substrate is baked at near the melting point of the fluoropolymer in order to improve its adhesion to the substrate.

8) The substrate is slowly cooled to about 200 °C by raising it above the surface of a heating device, such as a hot plate for example.

9) Finally, the substrate is cooled to an ambient temperature condition by using a chill plate.

If desired, the substrate may be planarized, imaged, and/or etched by employing conventional integrated circuit processing techniques which are known to those skilled in the art.

MICROEMULSION POLYMERIZATION PROCEDURE FOR PRODUCING SMALL PARTICLES OF POLYTETRAFLUOROETHYLENE

An aqueous microemulsion polymerization procedure produces unusually small particles of polytetrafluoroethylene (PTFE) which is particularly useful to form a low dielectric constant ILD in accordance with the teachings herein.

The ingredients, ratios and conditions of the microemulsion are selected to result in polymerization of liquid tetrafluoroethylene (TFE). In one aspect, the resulting polymers have a three-dimensional continuous micro-network of fibrils and bundles of fibrils and randomly dispersed platelets of TFE polymers. In another aspect, the resulting polymer produced is a gel characterized as a spongy mass comprised visually of layers of sheet-like configurations, and which has a microstructure of a three-dimensional continuous network of convoluted randomly disposed fibrils and bundles of fibrils of TFE polymers. In another aspect, the polymer produced is characterized as a spongy mass having a microstructure of predominantly randomly disposed platelets interconnecting or interpenetrating one another and also being randomly connected by randomly disposed fibrils, to form a three-dimensional continuous network of TFE polymer. In still another aspect, very small particles of TFE

polymer are produced. The form of the polymer produced depends on the ratio of surfactant to liquid TFE, as described above.

By microstructure, and the like, it is meant that the structure is not visible to the naked eye.

To form the polymers, a mixture of liquid tetrafluoroethylene (TFE) and at least one fluorinated surfactant in water is employed. The TFE may be introduced to the reaction vessel in liquid form, or in gaseous form and subsequently liquefied, in the presence of microemulsified seed particles, or micelles, of a liquid perfluorinated hydrocarbon that is a saturated aliphatic or aromatic organic compound having up to 2 oxygen, nitrogen, or sulfur atoms and a molecular weight preferably below 500.

PTFE produced from microemulsion polymerization when the surfactant/monomer ratio is at least 1.17 are usually small, being on the order of an average size of from 1 to 80 nanometers (0.001 to 0.080 micrometers), preferably 1 to 60 nanometers and most preferably 1 to 30 nanometers, and a polymer average molecular weight of over 100,000, preferably over 500,000 and most preferably over 1,000,000. It is believed that such unusually small polymer particles are obtained because polymerization of the gaseous TFE takes place inside the very small micelles of the hydrocarbon organic compound in the microemulsion.

The amount of surfactant used in the reaction is adjusted to maximize the formation of the type of particle desired, as described above. A suitable fluorinated surfactant or a mixture of fluorinated surfactants is needed with the weight ratio of the surfactants to monomers in the liquid phase of being adjusted according to the product desired. There is no criticality in an upper limit, but generally one usually does not go higher than 5:1. Suitable fluorinated surfactants include a fluorinated anionic surfactant, for example a salt of a fluorinated carboxylic acid or a sulfonic acid, a sulfate, a cationic surfactant for example a fluorinated quaternary ammonium salt, or a fluorinated nonionic surfactant. The mixture can be formed preferably at a temperature below the critical temperature (T_c) of TFE, approximately 33.3°C for TFE, and above the freezing temperature of the surfactant containing aqueous solution. Mechanical stirring can be provided. Free radical polymerization can be initiated by adding water-soluble free radical initiators, for example, a peroxide, an alkaline or ammonium persulfate, or some water soluble azo compounds or a salt of permanganate. The free radical initiators can also be used in association with a reducing agent such as ferrous salt, silver nitrate, sodium bisulfite, and the like. It is also possible to initiate the polymerization by photochemical reactions. The possible photoradiation source include ultraviolet (UV) light,

electron beam, or gamma radiation. The polymerization temperature can be between 5 to 100°C, and preferably between 5 to 33.3°C for polytetrafluoroethylene.

Comonomers that may be present in the mixture include halogenated (chlorine or fluorine) olefins of 2-18 carbon atoms, for example vinyl chloride, vinylidene chloride, chlorotrifluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ether, or the like; hydrogenated unsaturated monomers, such as ethylene, propylene, isobutylene, vinyl acetate, acrylates, or the like; crosslinking agents, such as glycidylvinylether, chloroalkyl vinyl ether, allyl-glycidylether, acrylates, methacrylates, or the like. The amount of comonomer that can be present should not be so great as to change the nature of the product that would be obtained if PTFE had been the product.

The perfluorinated hydrocarbon is a low molecular weight compound that is liquid at the temperature at which polymerization is carried out. The perfluorinated hydrocarbon preferably has a boiling point less than 230°C. The perfluorinated hydrocarbon can be a perfluorinated saturated aliphatic compound such as a perfluorinated alkane; a perfluorinated aromatic compound such as perfluorinated benzene, or perfluorinated tetradecahydrophenanthrene. It can also be a perfluorinated alkyl amine such as a perfluorinated trialkyl amine. It can also be a perfluorinated cyclic aliphatic, such as decalin; and preferably a heterocyclic aliphatic compound containing oxygen or sulfur in the ring, such as perfluoro-2-butyl tetrahydrofuran.

Examples of perfluorinated hydrocarbons include perfluoro-2-butyltetrahydrofuran, perfluorodecalin, perfluoromethyldecalin, perfluorodimethyldecalin, perfluoromethylcyclohexane, perfluoro(1,3-dimethylcyclohexane), perfluorodimethyldecahydronaphthalene, perfluorofluorene, perfluoro(tetradecahydrophenanthrene), perfluorotetracosane, perfluorokerosenes, octafluoronaphthalene, oligomers of poly(chlorotrifluoroethylene), perfluoro(trialkylamine) such as perfluoro(tripropylamine), perfluoro(tributylamine), or perfluoro(tripentylamine), and octafluorotoluene, hexafluorobenzene, and commercial fluorinated solvents, such as Fluorinert FC-75 which is produced by the 3M Company. The fluorinated alkanes can be linear or branched, with a carbon atom number between 3 and 20. Oxygen, nitrogen or sulfur atoms can be present in the molecules, but the number of such atoms per molecule should be 2 or less.

The preparation of the microemulsion depends on careful selection of the ingredients. The microemulsion is prepared by mixing water, perfluorinated hydrocarbon, fluorinated surfactant(s), and optionally cosolvents or inorganic salts. The amounts employed are 0.1-40

weight percent, preferably 0.1-20, of the perfluorinated hydrocarbon; 0.1-40 weight percent, preferably 0.1-25, of the surfactant; and optionally cosurfactants; with the remainder water. The microemulsified perfluorinated hydrocarbons are believed to serve as microreactors for fluorinated monomers to enter and to be polymerized. The temperature of the microemulsion formation can be between 0 to 150°C, preferably 40 to 100°C.

The fluorinated surfactant has the structure $R_fE X$, where R_f is a fluorinated alkyl group with a carbon number between 4 and 16, E is an alkylene group with a carbon number between 0 and 4, and X is an anionic salt such as $COOM$, SO_3M , SO_3NR_2 , SO_4M , a cationic moiety such as quaternary ammonium salt, or an amphoteric moiety such as aminoxide, or a non-ionic moiety such as $(CH_2CH_2O)_nH$; and M is H, Li, Na, K, or NH_4 ; R is a C_1 to C_5 alkyl group and n is a cardinal number of 2 to 40.

When tetrafluoroethylene is referred to herein, it is understood the term includes the so-called modified "homopolymer", in which the polymer chain includes very small amounts of units derived from perfluoro(propyl vinyl ether) or hexafluoropropylene.

To initiate polymerization, the temperature of the microemulsion is adjusted to between 0 and 150°C, preferably 40 to 100°C. Initiators for polymerization include free-radical initiators, such as persulfates, azo initiators, peroxides, or photo initiators which can generate free radicals by ultraviolet or gamma rays. Amount of initiators present can range between 0.001 to 5 percent by weight based on the final polymer content. Cosolvents such as an alcohol, amines or other amphiphilic molecules, or salt can be employed if desired to facilitate formation of the microemulsion.

Tetrafluoroethylene is introduced to the reactor from the vapor phase into the aqueous microemulsion phase. Sufficient mixing between liquid and vapor phase is important to encourage mass transfer. The mechanism of forming the ultra small polymer particles is not fully understood. It is believed that the higher the solubility of the tetrafluoroethylene monomer in the perfluorinated hydrocarbon, the better to achieve the original microemulsion particle size and shape. The time of reaction may be between 1 and 500 minutes.

The resulting polymer particles in the resulting dispersion have an average particle size of between 1 and 80 nanometers, preferably 1 to 60, most preferably 1 to 30, and a polymer average molecular weight of over 100,000, preferably over 1,000,000. The unusually small particle size provides a polymer system with a number of advantages over systems containing larger particles. The system is an aqueous colloidal dispersion, and is clear rather than turbid.

A small amount of units from comonomers may be present in the polymer, provided the amount of comonomer that can be present is not so great as to change the nature of the

product that would be obtained if PTFE had been the product. In other words, the copolymer is still not melt processible. The comonomer can be a halogenated (chlorine or fluorine) olefin of 2-18 carbon atoms, for example vinyl chloride, vinylidene chloride, chlorotrifluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ether, or the like; hydrogenated unsaturated monomers, such as ethylene, propylene, isobutylene, vinyl acetate, acrylates, or the like; crosslinking agents, such as glycidylvinylether, chloroalkyl vinyl ether, allyl-glycidylether, acrylates, methacrylates, or the like.

One suitable microemulsion for use as an ILD in accordance with the teachings herein had a weight ratio of surfactant to TFE liquid monomer of 330/230, i.e., well over 1.17. The resulting polymer was comprised of very small particles of PTFE, on the order of from about 0.001 to 0.06 micrometer. Such a material may be made by initially charging into a 10 liter pressure vessel, 5 Kg of deionized H₂O and 330g of ammonium perfluorooctanoate (Fluorad FC143, 3M). The pressure vessel was under vacuum and had been purged with tetrafluoroethylene gas by a vacuum repressive sequence three times. The oxygen content of the aqueous mixture was less than 20 ppm. The pressure vessel was cooled to be about 10°C and tetrafluoroethylene gas was fed into the reactor and some tetrafluoroethylene was allowed to condense into a liquid form in aqueous phase. Total amount of liquid tetrafluoroethylene charged to the pressure vessel was about 230g. The APFO/TFE ratio was over 1.17. The pressure vessel was equipped with a mixer and was used to stir the aqueous mixture at a speed of about 400 rpm. 2 grams of ammonium persulfate in 100g H₂O were charged to the vessel, followed by 1 gram of ferrous sulfate (FeSO₄) and 2 grams of sodium sulfite (Na₂SO₃) in 100g H₂O to initiate polymerization. The pressure inside the vessel was about 30 Kg/cm² starting from initiation to the end of about 2 hours reaction time. There was no significant pressure change throughout the reaction, which indicated that very little tetrafluoroethylene in the vapor phase participated the reaction. The temperature of the aqueous mixture inside the vessel was maintained between 10-12°C, employing brine water. After about 2 hours of reaction, tetrafluoroethylene gas was released from the vessel and the aqueous dispersion was discharged.

The aqueous dispersion looked clear, and contained about 4% polymer content. The melting temperature of the polymer was determined by Differential Scanning Calorimetry (DSC) to be about 331°C, which is in the melting range of polytetrafluoroethylene. The clarity of the dispersion is indicative of the presence of small particles on the order of 0.06 micrometer or less in size.

An ILD formed by a microemulsion of PTFE will have a dielectric constant of between 1.0 and 3.0.

**MICROEMULSION POLYMERIZATION PROCEDURE FOR
PRODUCING SMALL PARTICLES OF MELT PROCESSIBLE
FLUOROPOLYMER PARTICLES**

An aqueous microemulsion polymerization procedure produces unusually small particles of melt-processible fluoropolymers. During this procedure, the polymerization is carried out in the presence of microemulsified seed particles, or micelles, of a liquid perfluorinated hydrocarbon that is a saturated aliphatic or aromatic organic compound having up to two oxygen, nitrogen, or sulfur atoms and a molecular weight preferably below 500.

The polymer particles so produced are usually small, being on the order of one average size of 1 to 80 nanometers (0.001 to 0.080 micrometers), preferably 1 to 60 nanometers, and most preferably 1 to 30 nanometers. It is believed that such unusually small polymer particles are obtained because polymerization takes place inside the very small micelles of the hydrocarbon organic compound in the microemulsion.

The perfluorinated hydrocarbon is a low molecular weight compound that is liquid at the temperature at which polymerization is carried out. The perfluorinated hydrocarbon preferably has a boiling point less than 230°C. The perfluorinated hydrocarbon can be a perfluorinated saturated aliphatic compound such as a perfluorinated alkane, a perfluorinated aromatic compound such as perfluorinated benzene, or perfluorinated tetradecahydro phenanthrene. It can also be a perfluorinated alkyl amine such as a perfluorinated trialkyl amine. It can also be a perfluorinated cyclic aliphatic, such as decalin; and preferably a heterocyclic aliphatic compound containing oxygen or sulfur in the ring, such as perfluoro-2-butyl tetrahydrofuran. Suitable perfluorinated hydrocarbons are discussed above.

The preparation of the microemulsion depends on careful selection of the ingredients. The microemulsion is prepared by mixing water, perfluorinated hydrocarbon, fluorinated surfactant(s), and optionally cosolvents or inorganic salts. The amounts employed are 0.1-40 weight percent, preferably 0.1-20, of the perfluorinated hydrocarbon; 1-40 weight percent, preferably 0.1-25, of the surfactant; and optionally cosurfactants; with the remainder water. The microemulsified perfluorinated hydrocarbons are believed to serve as microreactors for fluorinated monomers to enter and to be polymerized. The temperature of the microemulsion formation can be between 0 to 150°C, preferably 40 to 100°C.

The fluorinated surfactant has the structure $R_fE X$, where R_f is a fluorinated alkyl group with a carbon number between 4 and 16, E is an alkylene group with a carbon number

between 0 and 4, and X is an anionic salt such as COOM, SO₃M, SO₃NR₂, SO₄M, a cationic moiety such as quaternary ammonium salt, or an amphoteric moiety such as aminoxide, or a non-ionic moiety such as (CH₂CH₂O)_nH; and M is H, Li, Na, K, or NH₄; R is a 1 to 5C alkyl group and n is a cardinal number of 2 to 40.

The polymerizable fluorinated monomers that are other than tetrafluoroethylene, include hexafluoroethylene, perfluoro alkyl vinyl ether, trifluoroethylene, vinylidene fluoride, vinyl fluoride, chlorotrifluoroethylene. Nonfluorinated monomers can be used as comonomers, such as vinylidene chloride, vinyl chloride, ethylene, propylene, butadiene. The monomer is preferably free-radical polymerizable, and preferably is ethylenically unsaturated.

To initiate polymerization, the temperature of the microemulsion is adjusted to between 0 and 150°C, preferably 40 to 100°C. Initiators for polymerization include free-radical initiators, such as persulfates, azo initiators, peroxides, or photo initiators which can generate free radicals by ultraviolet or gamma rays. Amount of initiators present can range between 0.001 to 5 percent by weight based on the final polymer content. Cosolvents such as an alcohol, amines or other amphiphilic molecules, or salt can be employed if desired to facilitate formation of the microemulsion.

The fluorinated gaseous monomers are introduced to the reactor from the vapor phase into the aqueous microemulsion phase. Sufficient mixing between liquid and vapor phase is important to encourage mass transfer. The mechanism of forming the ultra small fluorinated melt-processible polymer particles in this invention is not fully understood. It is believed that the higher the solubility of the monomers in the perfluorinated hydrocarbon, the better to achieve the original microemulsion particle size and shape. The time of reaction may be between 1 and 500 minutes.

The resulting polymer particles in the resulting dispersion have an average particle size of between 1 and 80 nanometers, preferably 1 to 60, most preferably 1 to 30. The unusually small particle size provides a polymer system with a number of advantages over systems containing larger particles. The system is an aqueous colloidal dispersion and is clear rather than turbid.

BICONTINUOUS MICROEMULSION POLYMERIZATION PROCEDURE FOR PRODUCING SMALL PARTICLES OF POLYTETRAFLUOROETHYLENE

One method of polymerizing liquid tetrafluoroethylene in an aqueous dispersion is described below and in U.S. Patents 5,399,640 and 5,403,900, which are incorporated herein by reference.

The ingredients, ratios and conditions are selected to result in polymerization of liquid tetrafluoroethylene (TFE) and optionally, minor amounts of other fluorinated ethylenically-unsaturated monomers that can be present. Free radical polymerization of the monomers produces polymers of tetrafluoroethylene. The polymers have a three-dimensional continuous micro-network of fibrils and bundles of fibrils and randomly dispersed platelets.

The polymer produced is a gel characterized as a spongy mass comprised visually of layers of sheet-like configurations, and which has a microstructure of a three-dimensional continuous network of convoluted randomly disposed fibrils and bundles of fibrils. The spongy mass may also have a microstructure of predominantly randomly disposed platelets interconnecting or interpenetrating one another and also being randomly connected by randomly disposed fibrils, to form a three-dimensional continuous network.

To form such polymers, a mixture of liquid tetrafluoroethylene (TFE) monomer and at least one fluorinated surfactant in water is employed. The TFE is introduced to the reaction vessel in liquid form and the amount of surfactant used in the reaction is adjusted to maximize the formation of a bicontinuous microemulsion system. It is believed that a bicontinuous microemulsion is formed spontaneously. A suitable fluorinated surfactant or a mixture of fluorinated surfactants is needed with the weight ratio of the surfactants to all monomers of from (in the liquid phase) at least 1:10, and preferably from 1:4 or 1:2 or higher in surfactant concentration. There is no criticality in an upper limit, but generally one usually does not go higher than 5:1. The amounts of the surfactants employed are from about 0.5 to about 50 weight percent, preferably from about 1 to about 20 percent; the amounts of total monomers (in the liquid phase) are from about 0.5 to about 50 weight percent; preferably from about 1 to about 30 percent; with the remainder water and optionally some salts. Suitable fluorinated surfactants include a fluorinated anionic surfactant, for example a salt of a fluorinated carboxylic acid or a sulfonic acid, a sulfate, a cationic surfactant for example a fluorinated quaternary ammonium salt; or a fluorinated nonionic surfactant. The mixture is formed at a temperature below the critical temperature (T_c) of TFE for example approximately 33.3 °C for TFE, and above the freezing temperature of the surfactant containing aqueous solution. Pressure should be below the critical pressure of TFE (i.e. below 39 atmospheres). Mechanical stirring can be provided. Free radical polymerization can be initiated by adding water-soluble free radical initiators, for example, a peroxide, an alkaline or ammonium persulfate, or some water soluble azo compounds or a salt of permanganate. The free radical initiators can also be used in association with a reducing agent such as ferrous salt, silver nitrate, sodium bisulfite, and the like. It is also possible to initiate the polymerization by

photochemical reactions. The possible photoradiation sources include ultraviolet (UV) light, electron beam, or gamma radiation. The polymerization temperature is below the critical temperature of polytetrafluoroethylene which is about 33.3 °C. A lower temperature can be any temperature above the freezing point of the mixture, but practically about 5 °C is preferred.

Comonomers that may be present in the mixture include halogenated (chlorine or fluorine) olefins of 2-18 carbon atoms, discussed above.

Free radical polymerization of the unsaturated monomers in such aqueous system can sometimes yield an aqueous medium containing colloidal fluorinated olefins having three-dimensional continuous network microstructure or can yield a spongy gel material.

Without intending to limit the scope of the present invention, the apparatus and method of production of the present invention may be better understood by referring to the following examples:

APPLICATION OF PTFE DISPERSION-NO ADHESION PROMOTER

Example 1

A 150 mm silicon wafer was spin coated with a microemulsion comprising 16% PTFE, 10% ammonium perfluorooctanoate and the balance comprised water. The average PTFE particle size was about 30 nanometers. The wafer was spun at 500 RPM, dried at 220 °C and sintered at 360 °C. Film thickness was about 0.75 microns as measured by SEM in cross-section.

Example 2

A 150 mm silicon wafer was spin coated with a microemulsion comprising 16% PTFE, 10% ammonium perfluorooctanoate, and the balance comprised water. The average PTFE particle size was about 30 nanometers. The wafer was spun at 1000 RPM, dried at 220 °C and sintered at 360 °C. Film thickness ranged from about 0.38 microns to about 0.40 microns, as measured by interferometry using a refractive index of 1.38, (using a NanoSpec 210 type interferometer from the NANOMETRICS Company).

Example 3

A 150 mm silicon wafer was spin coated with a microemulsion comprising 16% PTFE, 10% ammonium perfluorooctanoate, and the balance comprised water. The average PTFE particle size was about 30 nanometers. The wafer was spun at 2000 RPM, dried at 200 °C and sintered at 360 °C. Film thickness ranged from about 0.28 microns to about 0.30 microns,

as measured by interferometry using a refractive index of 1.38, (using a NanoSpec 210 type interferometer from the NANOMETRICS Company).

Example 4

A 150 mm silicon wafer was spin coated with a microemulsion comprising 16% PTFE, 10% ammonium perfluorooctanoate, and the balance comprised water. The average PTFE particle size was about 30 nanometers. The wafer was spun at 3000 RPM, dried at 200 °C and sintered at 360 °C. Film thickness ranged from about 0.21 microns to about 0.23 microns, as measured by interferometry using a refractive index of 1.38, (using a NanoSpec 210 type interferometer from the NANOMETRICS Company).

Example 5

A 150 mm silicon wafer was spin coated with a microemulsion comprising 16% PTFE, 10% ammonium perfluorooctanoate, and the balance comprised water. The average PTFE particle size was about 30 nanometers. The wafer was spun at 5000 RPM, dried at 200 °C and sintered at 360 °C. The average film thickness ranged from about 0.19 microns to about 0.22 microns, as measured by interferometry using a refractive index of 1.38, (using a NanoSpec 210 type interferometer from the NANOMETRICS Company).

Example 6

A 150 mm silicon wafer was spin coated with a bicontinuous microemulsion containing 10% PTFE, 7% ammonium perfluorooctanoate, and the balance comprised water. The wafer was spun at 500 RPM, dried at 200°C, and sintered at 360°C. The resulting coating was porous by SEM observation, and had a maximum thickness of 2 microns.

Referring to the Figures, Figure 1 is an SEM cross-section of a single crystal silicon wafer which has been coated with a PTFE microemulsion, in accordance with Example 1. The wafer was prepared by cleaving after immersing in liquid nitrogen. The bottom portion of Figure 1 is the cleaved silicon fracture surface. The middle portion of Figure 1 is the PTFE fracture surface. It is typical of low temperature, full density PTFE fracture surfaces. By scaling from the 100 nm measurement bar, the thickness is found to be approximately 0.75 microns. The top portion of Figure 1 is the "as deposited" PTFE surface. It is visible because the view is slightly less than perpendicular to the fracture surface. The surface is very smooth, flat, and pinhole free.

Figure 2 is an SEM surface view of a single crystal silicon wafer which has been coated with a bicontinuous PTFE microemulsion in accordance with Example 6. The PTFE is present in a series of full density nodes. These nodes are interconnected by PTFE fibrils. The PTFE closely resembles conventional expanded PTFE membranes. It differs in that it was

directly cast onto the surface of the wafer from the liquid microemulsion. Another method to achieve such an ILD would be to separately prepare, by a variety of extrusion and expansion processes, a PTFE membrane. This membrane would then have to be laminated onto the wafer. The teachings of the present invention eliminate many of such process steps. Also, the necessity to handle very thin membranes, which are fragile when not laminated to substrates, is eliminated by the teachings of the present invention.

Figure 3 is a graph of Deposited Film Thickness (Angstroms) v. Spin Speed (RPM) in accordance with the teachings of the present invention. It may be seen that thickness decreases smoothly with increasing rotational speed. This allows a variety of coating thicknesses in the range of from about 0.75 microns to about 0.2 microns to be easily deposited onto a substrate in accordance with the teachings herein.

Figure 4 is a graph of Isothermal Weight Loss Rate (%/minute) v. Temperature. This graph illustrates that the low dielectric material of the present invention is particularly useful as a dielectric material for an integrated circuit structure because of the low weight loss rates experienced by this material at the high temperatures which are required in the manufacture and processing of integrated circuit structures.

Thermal decomposition may be determined using any suitable conventional method. For example, thermal decomposition rate may be determined using a thermo-gravimetric analyzer (TGA) Model 2950 from TA Instruments, Inc. (New Castle, DE). A 50 mL sample of the microemulsion is placed in the 100 mL sample pan of the TGA. The sample pan is tared by the TGA prior to sample introduction. The majority of the solvent is allowed to evaporate at room temperature. This requires about two hours. Alternatively, the sample drying can be accelerated by placing the sample pan on a hot plate controlled at 80 to 90°C to avoid spattering the sample out of the pan by evaporating the liquid too rapidly. The sample and pan are cooled to room temperature. The sample is loaded into the TGA. (The instrument automatically hangs the pan from the hang-down wire of the balance.) The furnace is closed and the thermal method is started. The furnace and balance chamber are purged with dry nitrogen gas for at least two hours prior to running the first sample. The purge rate through the furnace is 60 mL/min and the balance chamber is 40 mL/min. It is important that both nitrogen purges be dried by passing the nitrogen gas through a Drierite® column prior to entering the TGA. (Drierite® is a registered trademark of W.A. Hammond Drierite Company.) As should be understood, nitrogen gas which has been taken from the boil-off of a liquid nitrogen tank is not dry enough for this test. It must still be passed through the Drierite® column prior to entering the TGA. The thermal method consists of: 1) heating the sample at

7.5°C/min, resolution = 4.0, to 250°C; 2) holding isothermal at 250°C for 30 mins; 3) heating at 7.5°C/min, resolution = 4.0, to 400°C; and 4) holding isothermal at 400°C for 120 mins. The data is analyzed by plotting only the last isotherm of the method as percent weight on the Y-axis and time (in minutes) on the X-axis. The percent weight at the start of this isothermal is adjusted to be 100 percent. This corrects for any residual solvent that may have been left in the sample after the initial drying step. Determining the curve value at the end of the isothermal curve (point 1) and sixty minutes prior to the end of the curve (point 2). Subtract the percent weight of point 1 from point 2 to obtain the percent weight loss per hour.

APPLICATION OF THE ADHESION PROMOTER

An adhesion promoter such as aminopropyl-triethoxysilane, and which is commercially available from DuPont as Paryline VM652, or hexamethyldisilazane (HMDS) is used. The VM652 or HMDS is applied to the silicon dioxide coated wafer by means of spin coating, although other methods may be used such as dipcoating, spraying, or evaporation coating.

Approximately 5 milliliters of VM652 or HMDS is dispensed onto the wafer while the wafer is rotating at a slow speed of approximately 50 RPM. The entire surface of the wafer is wetted with the adhesion promoter solution. The speed of the spin coater is then increased to between 1000 to 3000 RPM, most preferably 1000 RPM, until the adhesion promoter solvent has evaporated. This may be visually observed and typically occurs in about 30 seconds at 1000 RPM or 10 seconds at 3000 RPM. The adhesion promoter may then be dried at 130°C for 60 seconds. This drying step promotes the cross-linking of the silane molecule of the adhesion promoter to the SiO₂ coated substrate.

APPLICATION OF THE PTFE DISPERSION-WITH ADHESION PROMOTER

The dispersions may be coated onto the substrates by a number of methods, most preferably spin coating. Other methods include spraying, dipping, flowing, and meniscus coating.

A PTFE dispersion is applied to the SiO₂ coated substrate by the method of spin coating, although other methods may be used such as spraying or dipping. Typical PTFE dispersions which may be used are T30 from DuPont and D2 from Daiken. The PTFE dispersion is then applied to the adhesion promoter coated substrate in a similar method. A quantity of 5-10 milliliters of PTFE dispersion is dispensed onto the substrate while it spins at a slow speed of approximately 50 RPM. The entire surface of the substrate is wetted with the PTFE dispersion. The speed of the spin coater is then increased to between 500 and 5000

RPM to achieve the desired thickness of the dispersed film. The film may then be dried at a temperature of about 250°C to remove the residual water and surfactants, and finally the dried film is sintered at a temperature between 350°C and 390°C. This sintering step fuses together the PTFE particles. Most preferably, the sintering step is maintained for a period of 1 hour, although shorter treatments of as short as a few seconds may be used. The longer sintering treatments improve the adhesive bonds; however, this improvement in bond strength may not be necessary, depending on the application. The shorter sintering times may provide adhesive bond strength which is sufficient for the remainder of the device manufacturing and use conditions.

The adhesion of thin, submicron films on substrates is determined using the stud pull test. This test is recognized by leading semiconductor companies and by SEMATECH as a valid adhesion test method for thin films on substrates. Other techniques for evaluating the strength of adhesion include scratch testing, scotch tape testing per ASTM specification method D3359-93, thermal shock testing, bulge testing, and 4-point bend testing.

In the stud pull test, a small metal nail - or stud - is glued to the film. The stud is then pulled perpendicular to the film until the stud separates from the film or substrate. The load at which this failure occurs is then recorded and converted into a value of stress. The stress is calculated by dividing the force by the cross-sectional area of the adhesive bond of the stud to the substrate or film. The stud used in the test must be machined to very close tolerances. The stud surface that is glued to the substrate must be perpendicular to the shaft of the stud such that a straight pull may be achieved. In addition, the adhesive bond of the stud to the film surface should not be of lower strength than the adhesion of the film to the substrate. In addition, the adhesive must not contain any air bubbles that would reduce the cross-sectional area of the test, and the adhesive must be applied in a manner that insures that the adhesive does not seep out from underneath the stud and increase the cross-sectional area of the test.

For the purposes of evaluating stud pull adhesions of PTFE films, the PTFE film must be treated before the adhesive is applied in order to insure adequate adhesion of the stud adhesive. Most typically, this is done with the use of a brief oxygen plasma treatment followed by the deposition of a thin layer (about 1 micron) of SiO₂. The oxygen plasma treatment insures good adhesion of the SiO₂ to the PTFE, referred to as a cap layer. For the purpose of making integrated circuits and testing integrated circuit materials for adhesion, the use of the SiO₂ cap layer is preferred for adhesion testing because actual devices also will contain such an SiO₂ cap layer in many instances. Thus, performing the adhesive test with the SiO₂ cap layer is very similar to an actual integrated circuit device.

In order to complete the adhesion testing process of the PTFE coated substrate, the substrate is placed into a vacuum chamber and subjected to a brief oxygen plasma etch. In this invention, the etching was done in a Plasmatherm 7000 series reactive ion etching unit. The etch gas was oxygen at a flow rate of 400 SCCM, a chamber pressure of 150 millitorr, and a power of 500 watts. The etching is typically conducted for a period of 15 seconds. The etched substrate is then coated with SiO_2 in a Plasmatherm 7000 series CVD reactor with a flow rate of 400 SCCM silane, 1400 SCCM nitrous oxide, a chamber pressure of 100 millitorr, and a process power of 500 watts. Aluminum studs with a diameter of 4.5 MM were then glued to samples of the substrates using an epoxy adhesive, such as Araldite adhesive from Super Glue Corporation. The samples were then left to cure for a period of about 24 hours. Adhesion testing was then performed on a Dage microtester 22. Failure of load values were recorded and then converted into stress values.

A 1 micron thick oxide layer was applied to 6 bare silicon wafers in a Plasmatherm 700 series CVD reactor with a gas flow rate of 400 SCCM silane, 1400 SCCM nitrous oxide, a chamber pressure of 100 millitorr, and a power of 500 watts. APTS was applied to 2 wafers using a spin coater. The wafers were spun for 10 seconds at 50 rpm to allow a manual dispense of APTS. After the wafers were wetted thoroughly with the APTS the wafers were then spun for 30 seconds at 1000 rpm to remove all excess material and allow the promoter solvent to evaporate. The wafers were then passed onto a hot plate set at a temperature of 130°C with direct contact for 60 seconds to allow curing of the APTS, and then were cooled on a chill plate (~13°C) for 10 seconds.

HMDS was applied to 2 wafers using a similar procedure. The wafers were spun for 10 seconds at 50 rpm to allow a manual dispense of the HMDS. After the wafers were wetted thoroughly with the HMDS the wafers were then spun for 30 seconds at 1000 rpm to remove all excess material and allow the promoter solvent to evaporate. The wafers were then baked in an oven under N_2 purge for 1 hour at 200°C.

The PTFE dispersions T-30 and D-2 were also applied using the spin coater. All 6 wafers were spun for 10 seconds at 50 rpm to allow a manual dispense of the PTFE. After the wafers were wetted thoroughly with the PTFE the wafers were allowed to sit for 10 seconds. The wafers were then spun for 45 seconds at 920 rpm to remove all excess material and allow the water to evaporate. The wafers were then passed to a hot plate operating at a temperature of 250°C. The wafers were allowed to preheat for 30 seconds at a setting of 20 steps above the hot plate and then direct contact for 60 seconds to bake off the surfactant. The baked wafers were then sintered at 390°C for 5 minutes and immediately cooled on a chill

plate (~130°C) for 15 seconds. A surface treatment was applied to the wafers in a Plasmatherm 7000 series reactive ion etching unit with oxygen as the etch gas at a flow rate of 150 SCCM, a chamber pressure of 100 millitorr, and a power of 125 watts with an exposure time of 50 seconds. A final SiO₂ cap (1 micron thick) was then applied to the wafers in a Plasmatherm 7000 series CVD reactor with a flow rate of 400 SCCM silane, 1400 SCCM nitrous oxide, a chamber pressure of 100 millitorr, and a power of 500 watts.

The wafers were cleaved into squares of a surface area of 1 cm² to 1 in². Metal studs of surface areas 0.025 in² were glued perpendicular to the stud shaft onto these squares using Quick Setting Epoxy by Super Glue Corporation. It was essential that only the amount of glue needed to completely cover the end of the stud was applied. The samples were allowed to cure for a period of at least 24 hours. The Series 22 Microtester by Dage measured the failure loads of approximately 10 samples from each wafer. Some samples were thrown out if the test results due to 2 reasons. In preparation of the epoxy it was necessary to mix equal parts of resin and adhesive. The method used was not quantitative and it appeared that one batch of mixture did not contain enough of one ingredient to allow the epoxy to set, causing little or no adhesion. The second reason was an excess amount of epoxy applied to the stud. Too much epoxy squeezed form underneath the stud causing a greater contact surface area and therefore the test on that sample was unacceptable.

ADHESION AND T TEST

The results of the stud pull test are shown in the Tables below. Both APTS and HMDS provided improved adhesion for each PTFE dispersion, with APTS providing better results than HMDS. A T-test was applied to all possible combinations within each PTFE dispersion.

TABLE 1

ADHESION TESTS OF D-2 AND T-30

D-2 WITH NO ADHESION PROMOTER

kg	lbs	psi	in ²	S.dev	Ave(psi)	Sample
1.90	4.19	167.55	0.025	35.411	133.380	8
1.30	2.87	114.64				
1.50	3.31	132.28				
1.70	3.75	149.91				
1.60	3.35	141.10				
1.10	2.43	97.00				
0.90	1.98	79.37				
2.10	4.63	185.19				

D-2 APTS

kg	lbs	psi	in ²	S.dev	Ave(psi)	Sample
1.90	4.19	167.55	0.025	56.885	247.898	8
2.10	4.63	185.19				
2.80	6.17	246.92				
2.80	6.17	246.92				
3.60	7.94	317.47				
3.50	7.72	308.65				
2.70	5.95	238.10				
2.30	5.07	202.83				
3.60	7.94	317.47				

D-2 HMDS

kg	lbs	psi	in ²	S.dev	Ave(psi)	Sample
2.20	4.85	194.01	0.025	53.277	163.142	10
0.80	1.76	70.55				
0.70	1.54	61.73				
2.20	4.85	194.01				
2.00	4.41	176.37				
2.00	4.41	176.37				
2.20	4.85	194.01				
2.00	4.41	176.37				
1.90	4.19	167.55				
2.50	5.51	220.46				

T-30 NO ADHESION PROMOTER

kg	lbs	psi	in ²	S.dev	Ave(psi)	Sample
0.30	0.68	26.46	0.025	35.548	70.548	9
1.00	2.20	88.18				
0.50	1.10	44.09				
0.40	0.88	35.27				
1.00	2.20	88.18				
1.60	3.53	141.10				
1.00	2.20	88.18				
0.80	1.76	70.55				
0.60	1.32	52.91				

T-30 APTS

kg	lbs	psi	in ²	S.dev	Ave(psi)	Sample
3.80	8.38	335.10	0.025	68.459	338.630	10
2.50	5.51	220.46				
4.60	10.14	405.65				
3.00	6.61	264.55				
3.50	7.72	308.65				
3.60	7.94	317.47				
3.60	7.94	317.47				
4.90	10.80	432.11				
4.10	9.04	361.56				
4.80	10.58	423.29				

T-30 HMDS

kg	lbs	psi	in ²	S.dev	Ave(psi)	Sample
1.80	3.97	158.73	0.025	85.425	221.565	8
3.70	8.16	326.28				
2.20	4.85	194.01				
2.10	4.63	185.19				
1.40	3.09	123.46				
2.00	4.41	176.37				
2.70	5.95	238.10				
4.20	9.26	370.38				

T TESTSD-2 PTFE DISPERSION

	none	APTS	HMDS	
none		13.552	15.577	D.O.F.
APTS	5.039937		16.485	
HMDS	1.417914	3.341413		

T-30 PTFE DISPERSION

	none	APTS	HMDS	
none		13.806	9.132	D.O.F.
APTS	22.62394		13.308	
HMDS	12.74457	3.87603		

D-2 %certainty

None-APTS 99.95%

None-HMDS 99.95%

APTS-HMDS 99.75%

The % certainty is the certainty that the two groups came from different distributions.

T-30

None-APTS 99.95%

None-HMDS 99.95%

APTS-HMDS 99.80%

Measuring the dielectric constant of thin films is difficult. More particularly, in many types of thin films, the dielectric constant is not isotropic, i.e., the dielectric constant is often lower through the thickness (z-axis) of the film than it is in-plane (xy-plane). Thus, while many reported values of low dielectric constant materials report only the through thickness result, it is the in-plane dielectric constant that is important for the application of an integrated circuit dielectric material. The xy-plane dielectric constant determines the line-to-line capacitance, which is the dominant component of capacitive delay in integrated circuits.

Typically, measurement of dielectric constant in the z-axis is performed through the use of a metal-insulator-metal (MIM) parallel plate capacitor structure. The dielectric constant is calculated by determining the capacitance of the MIM structure. For the dielectric constant to be calculated accurately, it is important that both the area of the MIM and the insulator thickness be known. Often, it is difficult to determine the precise thickness of the insulated layer. Additionally, another common technique employed to measure dielectric constant in the z-axis uses a liquid mercury probe as the upper metal surface. Use of the mercury probe is simple; however, its use is complicated by the fact that the actual mercury probe contact area is not well known. It can vary greatly since the mercury has an extremely high surface tension and does not reproducibly wet the same surface with the same contact area.

At times, the dielectric constant of material is reported as a simple square of the material's index of refraction. This type of dielectric constant measurement permits calculation of dielectric constant both in the xy-plane and the z-axis of a thin film. However, such a dielectric constant measurement is determined at optical frequencies which is significantly different from the dielectric constant of the material at typical frequencies used in electronic signal propagation. As is well known, measurement of the dielectric constant by the simple square of the index of refraction typically understates the dielectric constant by an amount equal to approximately 0.2.

The following method may be employed to determine the xy-plane dielectric constant of an integrated circuit dielectric element of the present invention.

A base substrate, such as silicon or a silicon dioxide, is metallized typically with aluminum or copper by sputtering, MOCVD, or electroplating. The metallized substrate is then coated with a dielectric material. A typical coating thickness is approximately 1 micron, although other thicknesses can be used provided they do not demonstrate a change in critical properties, such as isotropy. A small portion of the metallized substrate is masked off prior to

dielectric deposition to permit contacting the metallized substrate surface during testing. Following deposition of the dielectric layer, another metallic layer with a simple pattern is deposited on top of the dielectric material. A 1 cm x 1 cm square pattern is masked on the dielectric material through the use of a tape such as polyimide tape. Once the 1 cm x 1 cm area is defined with the tape, the substrate is then metallized again with a similar process such as sputtering or MOCVD or electroplating.

After metallization, the polyamid tape is removed from the dielectric in order to leave behind a 1 cm x 1 cm metallization on the top surface of the wafer. The capacitance between the 1 cm x 1 cm top layer of metal on the base substrate is then measured through the use of an instrument such as a Hewlett-Packard Model 4284 LCR meter. The precise film thickness is then determined by a scanning electron microscopy cross-section photomicrograph, unless other more accurate and verified methods can be shown for the dielectric material being tested. The dielectric constant is then calculated from the measured capacitance and thickness of the sample. This determines the dielectric constant in the z-axis.

Next, the xy-plane and z-axis index of refraction is measured through the use of a prism coupler, such as that manufactured by Metrocon, Inc. The index of refraction in the z-axis and the xy-plane are then both squared. The squared number for the xy-plane index of refraction is then subtracted from the square of the index of refraction for the z-axis. This difference is then subtracted from the previously calculated value for the dielectric constant of the z-axis direction to determine the dielectric constant of the xy-plane.

Although a few exemplary embodiments of the present invention have been described in detail above, those skilled in the art readily appreciate that many modifications are possible without materially departing from the novel teachings and advantages which are described herein. Accordingly, all such modifications are intended to be included within the scope of the present invention, as defined by the following claims.

CLAIMS:

Having described the invention, what is claimed is:

1. A method of bonding a fluoropolymer film comprising:
treating a substrate bearing at least one of metal, alloy and semiconductor feature with a silane compound, and thereafter coating the substrate with a fluoropolymer dielectric material.
2. The method according to claim 1, wherein said dielectric material is formed from a nanoemulsion.
3. The method according to claim 1, wherein said silane is a alkoxysilane or silazane.
4. The method according to claim 1, wherein an aminoalkylalkoxy silane is used and the alkyl and alkoxy moieties have a C₁-C₆ chain length.
5. The method according to claim 4, wherein said alkyl moiety of said aminoalkylalkoxy silane is at least one C₁ to C₄ alkyl group and said alkoxy is a C₁ to C₄ alkoxy group.
6. The method according to claim 1, herein said silane compound is,
aminopropyltrimethoxysilane,
aminopropyltriethoxysilane,
aminoethyltrimethoxy silane,
methylaminopropyltrimethoxysilane,
aminopropyltripropoxysilane,
aminopropylmethyldiethoxysilane,
aminopropylethyldiethoxysilane,
aminomethyltriethoxysilane,
aminoisobutyltrimethoxysilane,
aminobutyltriethoxysilane,
beta-aminoethyltriethoxysilane,
aminobutylmethyldiethoxysilane,
(aminoethylaminomethyl)-phenethyltrimethoxysilane,
(aminoethylaminomethyl)-phenethyltriethoxysilane,

n-(aminoethyl)-aminopropyl-methyldimethoxysilane,
n-(aminoethyl)-aminopropyl-methyldiethoxysilane,
n-(aminoethyl)-aminopropyl-trimethoxysilane,
n-(aminoethyl)-aminopropyl-triethoxysilane,
p-aminophenyltrimethoxysilane,
p-aminophenyltriethoxysilane,
n-phenylaminopropyltrimethoxysilane,
n-phenylaminopropyltriethoxysilane,
(trimethoxysilylpropyl)diethylenetriamine,
(triethoxysilylpropyl)diethylenetriamine,
aminopropyldimethylmethoxysilane,
aminopropyldimethylethoxysilane,
phenylaminotriethoxysilane,
phenylaminotrimethoxysilane,
phenylaminotripropoxysilane,
hexamethyldisilazane,
tetraethoxysilane,
tetramethoxysilane, or
tetrapropoxysilane.

7. The method according to claim 5, wherein said aminoalkylalkoxy silane is aminopropyltriethoxysilane.
8. The method according to claim 3, wherein 0.05 to 10 wt. % of said aminoalkylalkoxy silane in a solvent is applied to the substrate.
9. The method according to claim 8, wherein said solvent is at least one of water, a C₁ to C₃ alcohol and 1-methoxy-2-propanol.
10. The method according to claim 1, wherein the fluoropolymer dielectric dispersion is applied to form a layer having a dielectric constant in a range from about 1.3 to about 2.2.
11. The method according to claim 1, wherein the thickness is less than 1.5 μ m.

12. The method according to claim 1, wherein the fluoropolymer dielectric material has a weight loss is less than 0.15%/ minute at 420 °C.
13. The method according to claim 1, wherein the weight loss is less than 0.02%/ minute at 420 °C.
14. The method according to claim 1, wherein the fluoropolymer is a homopolymer of tetrafluoroethylene.
15. The method according to claim 1, wherein the fluoropolymer is a copolymer of tetrafluoroethylene.
16. The method according to claim 1, wherein the fluoropolymer includes comonomers selected from a group consisting of hexafluoropropylene and perfluoro (alkyl vinyl ether).
17. The method according to claim 1, wherein the fluoropolymer further includes antioxidants.
18. The method according to claim 1, wherein the fluoropolymer further includes silicon dioxide.
19. The method according to claim 1, wherein the fluoropolymer is porous.
20. A multilayer insulative material, comprising:
at least first and second chemically disparate layers, said first layer containing a silane and said second layer containing at least one fluoropolymer layer having a weight loss of less than 0.15%/minute at 420 °C and a thickness of less than 5µm.
21. The multilayer insulative material according to claim 20, wherein the fluoropolymer layer has a dielectric constant in a range from about 1.3 to about 2.2.
22. The multilayer insulative material according to claim 20, wherein the fluoropolymer layer thickness is less than 1.5µm.
23. The multilayer insulative material according to claim 20, wherein the weight loss is less than 0.02%/minute at 420 °C.

24. The multilayer insulative material according to claim 20, wherein the weight loss is less than 0.01%/minute at 420 °C.
25. The multilayer insulative material according to claim 20, wherein the fluoropolymer is a homopolymer of tetrafluoroethylene.
26. The multilayer insulative material according to claim 20, wherein the fluoropolymer is a copolymer of tetrafluoroethylene.
27. The multilayer insulative material according to claim 20, wherein the fluoropolymer includes comonomers selected from a group consisting of hexafluoropropylene and perfluoro (alkyl vinyl ether).
28. The multilayer insulative material according to claim 20, wherein the fluoropolymer further includes antioxidants.
29. The multilayer insulative material of claim 20, wherein the fluoropolymer further includes silicon dioxide.
30. The multilayer insulative material according to claim 20, wherein the fluoropolymer is porous.
31. An electronic device:
at least one semiconductor component;
a superimposed adhesion promoting layer; and
at least one superimposed fluorinated polymer layer having a dielectric constant of less than 2.2, a weight loss of less than 0.15%/minute at 420 °C, a thickness of less than 5 μ m, and a retention strength greater than 200 psi.
32. The device according to claim 31, wherein said adhesion promoter is a silane.
33. The device according to claim 32, wherein said silane is an alkoxy silane or silazane.

34. The device according to claim 32, wherein said silane is an aminoalkylalkoxy silane and the alkyl and alkoxy moieties have a C₁-C₆ chain length.
35. The device according to claim 34, wherein said alkyl moiety of said aminoalkylalkoxy silane is at least one C₁ to C₄ alkyl group and said alkoxy is a C₁ to C₄ alkoxy group.
36. The device according to claim 31, wherein said adhesion promoter is,
- aminopropyltrimethoxysilane,
 - aminopropyltriethoxysilane,
 - aminoethyltrimethoxy silane,
 - methylaminopropyltrimethoxysilane,
 - aminopropyltripropoxysilane,
 - aminopropylmethyldiethoxysilane,
 - aminopropylethyldiethoxysilane,
 - aminomethyltriethoxysilane,
 - aminoisobutyltrimethoxysilane,
 - aminobutyltriethoxysilane,
 - beta-aminoethyltriethoxysilane,
 - aminobutylmethyldiethoxysilane,
 - (aminoethylaminomethyl)-phenethyltrimethoxysilane,
 - (aminoethylaminomethyl)-phenethyltriethoxysilane,
 - n-(aminoethyl)-aminopropyl-methyldimethoxysilane,
 - n-(aminoethyl)-aminopropyl-methyldiethoxysilane,
 - n-(aminoethyl)-aminopropyl-trimethoxysilane,
 - n-(aminoethyl)-aminopropyl-triethoxysilane,
 - p-aminophenyltrimethoxysilane,
 - p-aminophenyltriethoxysilane,
 - n-phenylaminopropyltrimethoxysilane,
 - n-phenylaminopropyltriethoxysilane,
 - (trimethoxysilylpropyl)diethylenetriamine,
 - (triethoxysilylpropyl)diethylenetriamine,
 - aminopropyldimethylmethoxysilane,
 - aminopropyldimethylethoxysilane,
 - phenylaminotriethoxysilane,

phenylaminotrimethoxysilane,
phenylaminotripropoxysilane,
hexamethyldisilazane,
tetraethoxysilane,
tetramethoxysilane, or
tetrapropoxysilane.

37. The device according to claim 34, wherein said aminoalkylalkoxy silane is aminopropyltriethoxysilane.
38. The device according to claim 31, wherein the dielectric constant is in a range from about 1.3 to about 2.2.
39. The device according to claim 31, wherein the thickness is less than 1.5 μ m.
40. The device according to claim 31, wherein the weight loss is less than 0.02%/minute at 420 °C.
41. The device according to claim 31, wherein the weight loss is less than 0.01%/minute at 420 °C.
42. The device according to claim 31, wherein the fluorinated polymer is a homopolymer of tetrafluoroethylene.
43. The device according to claim 31, wherein the fluorinated polymer is a copolymer of tetrafluoroethylene.
44. The device according to claim 31, wherein the fluorinated polymer includes comonomers selected from a group consisting of hexafluoropropylene and perfluoro (alkyl vinyl ether).
45. The device according to claim 31, wherein the fluorinated polymer further includes antioxidants.

46. The device according to claim 31, wherein the fluorinated polymer further includes silicon dioxide.
47. The device according to claim 31, wherein the fluorinated polymer is porous.

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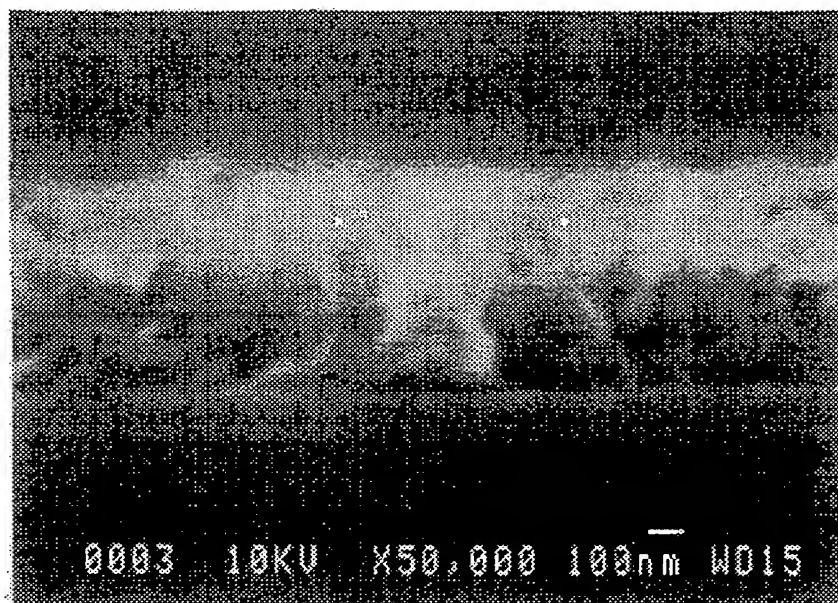


FIG.1

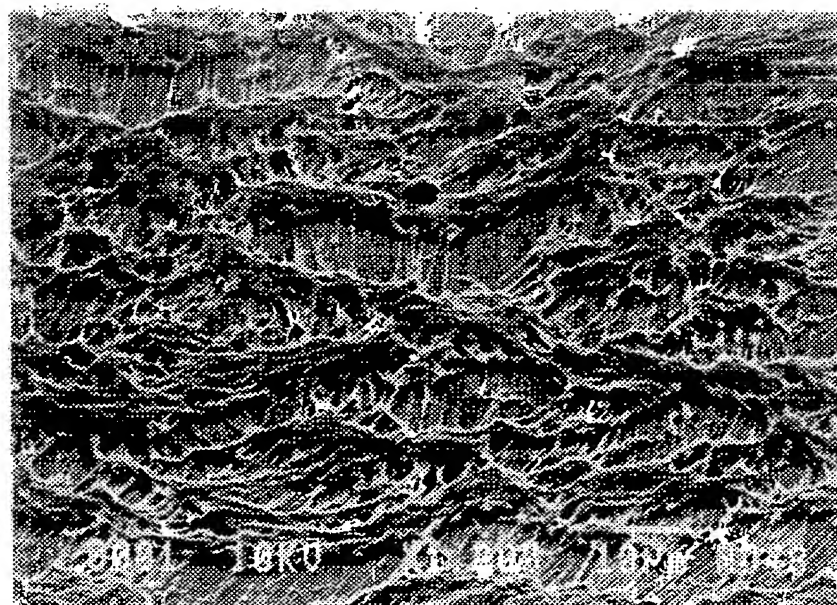
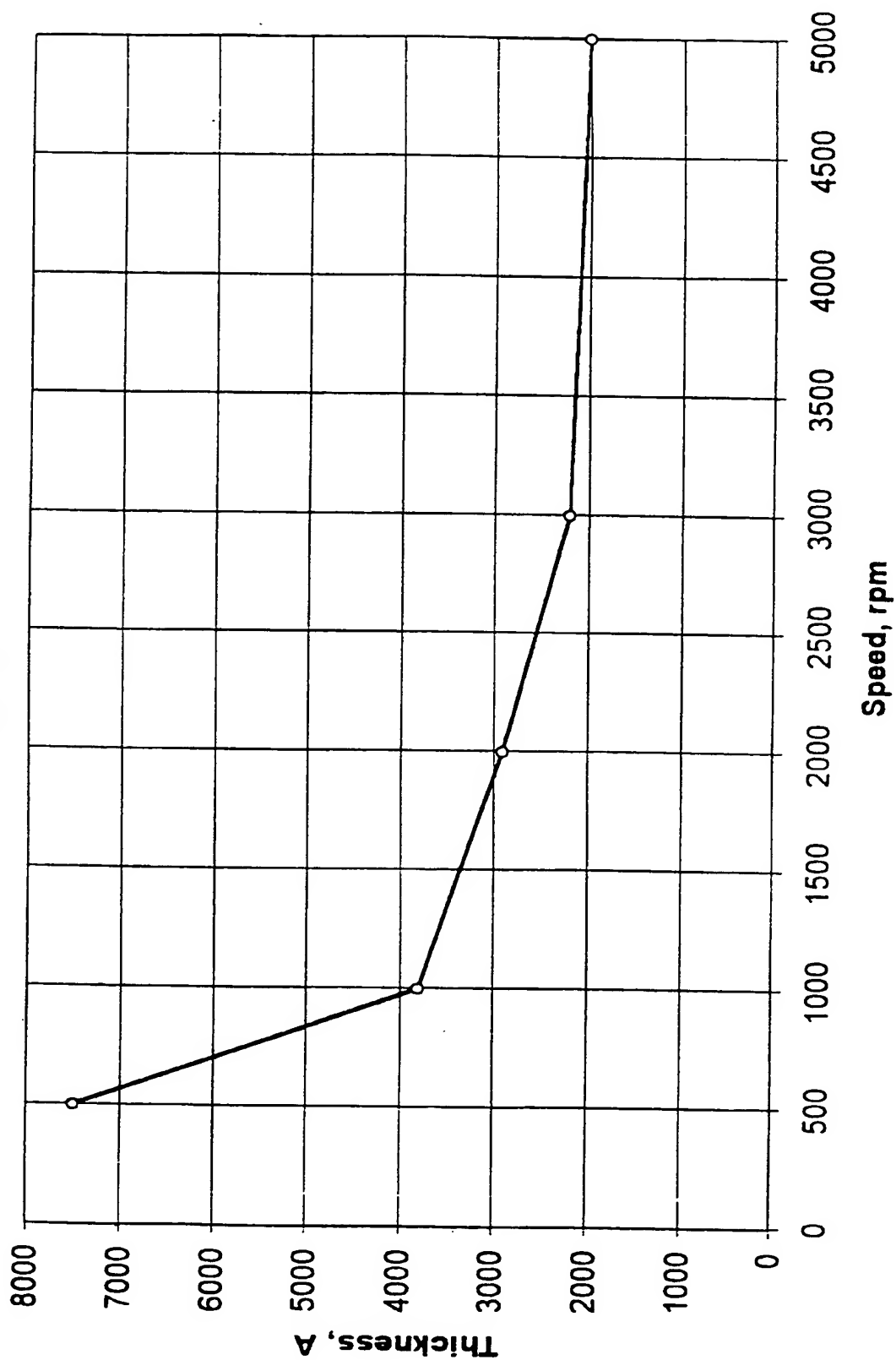


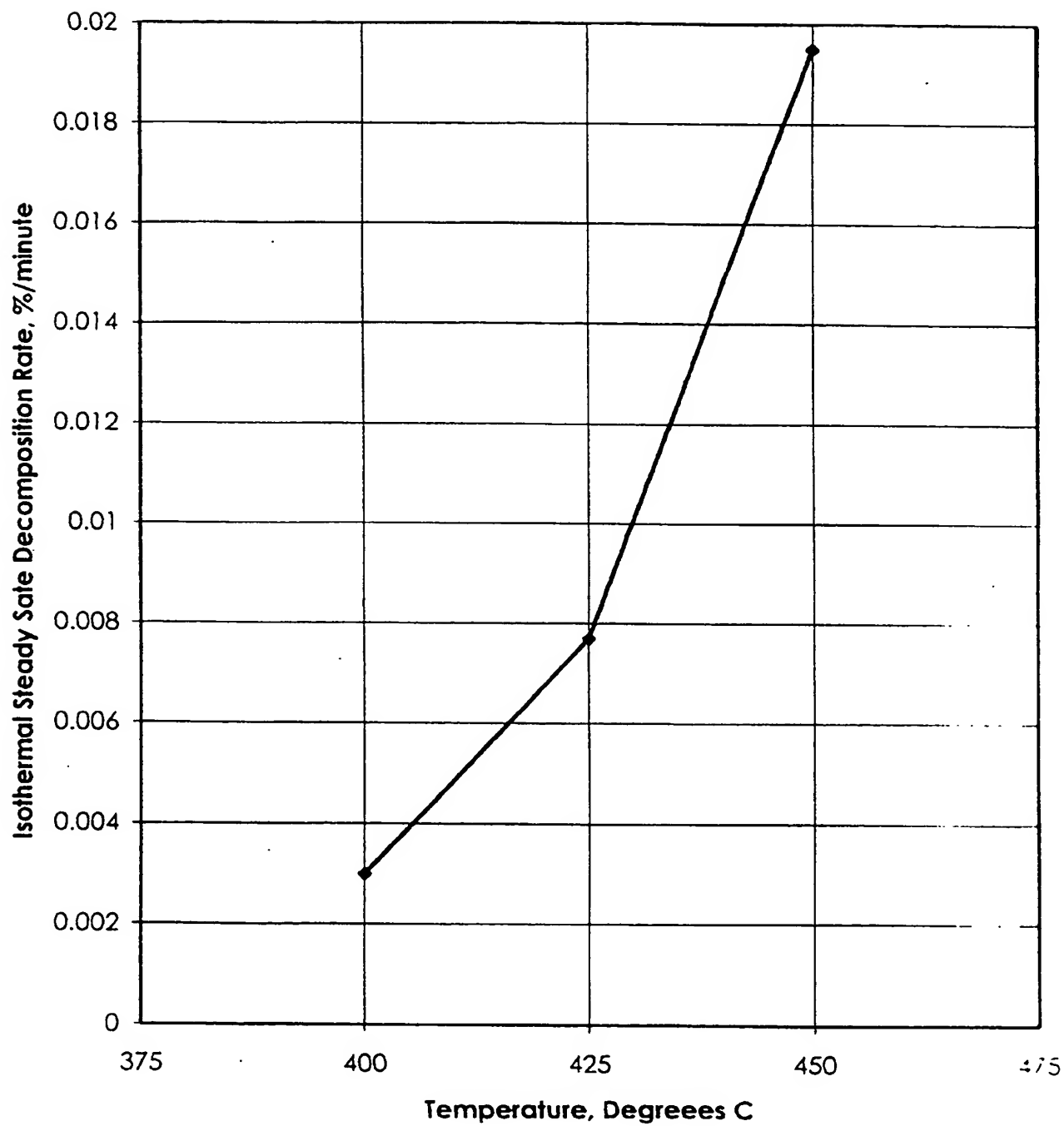
FIG.2

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FIG. 3



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FIG. 4

INTERNATIONAL SEARCH REPORT

Inte Application No

PCT/US 98/01461

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01L21/312 H01L21/768 H01L23/532 B05D5/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01L B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	DE 19 54 233 A (DU PONT) 9 July 1970 see page 2, line 16 - line 23; tables 1-6	1,3-5 2,12-14, 19-25, 31-35, 38-42
Y	ROSENMYER T ET AL: "PTFE nanoemulsions as spin-on, low dielectric constant materials for ULSI applications" ADVANCED METALLIZATION FOR FUTURE ULSI. SYMPOSIUM, ADVANCED METALLIZATION FOR FUTURE ULSI. SYMPOSIUM, SAN FRANCISCO, CA, USA, 8-11 APRIL 1996, 1996, PITTSBURGH, PA, USA, MATER. RES. SOC, USA, pages 463-468, XP002063620 see the whole document	2,12-14, 19-25, 31-35, 38-42

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

7 May 1998

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/01461

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 440 805 A (DAIGLE ROBERT C ET AL) 15 August 1995 see column 5, line 20 - line 40; claims 1-36; figures 1-11 ---	1, 29, 31, 46
A	EP 0 736 583 A (DAIKIN IND LTD) 9 October 1996 see the whole document ---	1-3
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 5842257, SUN S C ET AL: "Evaluation of PTFE nanoemulsion as a low dielectric constant material ILD" XP002064283 see abstract & LOW-DIELECTRIC CONSTANT MATERIALS II. SYMPOSIUM, LOW-DIELECTRIC CONSTANT MATERIALS II. SYMPOSIUM, BOSTON, MA, USA, 2-3 DEC. 1996, ISBN 1-55899-347-9, 1997, PITTSBURGH, PA, USA, MATER. RES. SOC, USA, pages 85-90, XP002063619 ---	
A	US 5 549 935 A (NGUYEN THAO N ET AL) 27 August 1996 see the whole document -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter Application No

PCT/US 98/01461

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 1954233 A	09-07-70	CA 918515 A FR 2021850 A GB 1285726 A NL 6916307 A US 3787281 A	09-01-73 24-07-70 16-08-72 04-05-70 22-01-74
US 5440805 A	15-08-95	US 5287619 A EP 0645952 A JP 7170069 A EP 0560077 A	22-02-94 29-03-95 04-07-95 15-09-93
EP 0736583 A	09-10-96	JP 8120211 A US 5712335 A WO 9612773 A	14-05-96 27-01-98 02-05-96
US 5549935 A	27-08-96	JP 1967878 C JP 4329638 A JP 6101462 B	18-09-95 18-11-92 12-12-94

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